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Abstract

The secondary lithium battery which is the silicon material powder in which the anodal active material contains the boron as to the secondary lithium battery containing the anodic active material, and the anodal active material and non-aqueous electrolyte, and contains the boron with 50 weight% through 0.1.



Description

■ Details of the Invention

■ Purpose of the Invention

- The Technical Field to which the Invention belongs and the Prior Art in that Field

The present invention relates to the active material for the secondary lithium battery and the thus used cathode. More concretely, the present invention relates to the active material for the high-end secondary lithium battery in which moreover, the capacity loss in a charging/discharging is less the discharge capacity is big it has the high voltage and the thus used cathode.

The present invention relates to the secondary lithium battery using the active material for a cathode and this having the initial efficiency which is high in excess of moreover, the theory capacity of the graphite, and the cycleability of being excellent.

- The Technical Challenges of the Invention

The secondary lithium battery has the high energy density. Therefore, it is used as the group special mobile communication, and the power source for the portable information end. The market rapidly expands with the supply of the terminal.

Thus, it accompanies and the graphite system carbonaceous material as the special activity material of the terminal equipment has the high discharge capacity exceeding 300mAh / g/6, and the high initial efficiency more than 90%. Moreover, swelling and shrinking accompanied with the insertion deintercalation between the black lead layer surface of the lithium ion at a charging/discharging are lower than about 10%. The deterioration of the amount of discharge accompanied with the rechargeable cycle is considerably low. The discharge capacity more than 50% can be preserved through the charging/discharging of 500 time. In this way, the graphite system carbonate material provides the property that is desirable as the active material for the lithium ion secondary battery cathode.

But as to the amount, which reversibly can insert the lithium among the material and escape the lithium 1 atom is a limit about the carbon 6 atom. 372mAh / g/6 is the theoretical marginal volume toward the charging/discharging of the carbon material as the electric capacity. Whether it limps with the existing second or not is used in the level which is near to this marginal volume. Therefore, the remarkable performance improvement of an afterward cannot expect. But the continuous capacity enhancement is expected about the existing secondary battery. The high initial efficiency, of the graphite system carbonaceous material widely employed in the practical cell the expansion shrinkage which is low as to a charging/discharging, and the cycleability of being high are maintained. The development of the active material material for the cathode having the high discharge capacity exceeding the theory capacity of the graphite is demanded.

The search about the material having the capacity which is 372mAh / g/6 more than as a material except a carbon, for example, the inorganic compound including an alloy or an oxide etc. is gradually achieved under this kind of situation. Among them, it discovered to exhibit the crystalline including specially, the tin, and silicon, and the discharge capacity which was near to 1000mAh / g/6 to the amorphous oxide material (for example, JP-A-07-220721, JP-A-07-249409 etc). Moreover, recently, in case the silicon group (單??) was used for the anodal active

material, the initial discharge capacity of 3000mAh / g either before or after was shown. In case the silicon oxide was used as the anodal active material, the initial discharge capacity of 1500mAh / g either before or after was shown (the 38 time battery forum, and 3A17 (1997)). It was reported to have the discharge capacity which more jumped over the marginal volume of the graphite system carbonaceous material. But any kind of material against the initial discharge capacity the initial charging capacity severed. That is, the capacity loss in a charging/discharging was considerably big. A thing of a cycleability the day (the capacity with the number cycle after the charging/discharging initiation is the reduction by half) was the big (about both material, altogether, 1000mAh / g) problem.

In the meantime, as the material including the boron in the silicon, the boron compound powder (JP-A-08-138744, USP5571637) of the silicon in which 3 persons the boridation silicon alloy structure (JP-A-53-136630), and a n of a n is principal from 0.1 from 3.2 with the SiB_n this of the range of 6.6 is disclosed as to the general equation SiB_n .

In the alloy structure, the big discharge capacity which more jumped over the graphite system carbonaceous material of the silicon inherent was shown. But the concentrator matrix was precipitated among the alloy bath and it was the electrode undergone plastic surgery. Therefore, recently, when the active material powder on the charge collecting film like looking the lithium ion battery put to practical use is compared with the electrode which it coats with a binder to make with the slurry and it undergoes plastic surgery, it was difficult for the mass production. Moreover, it is difficult. Therefore, what makes the film thickness thin the diffusion of the lithium within an electrode is not enough obtained under the big electric current density. The alloy structure looked at brings about the big polarization resistance. It enough cannot take out the occlusion one lithium. Therefore, it has a reversibility with the big problem the capacity loss in a charging/discharging is enlarged. In the meantime, it was difficult to the boron compound powder of the silicon deciding on the latter SiB_n etc. to the subject to obtain the discharge capacity higher than the graphite system carbonaceous material.

In WO98/24135, the material for cathode heat-treating the silicon or the compound under the presence of the organic material or the carbon material and was obtained was disclosed. But it was material consisting of the silicon and carbon. Therefore, considerably big swelling and shrinking problem of being accompanied with the charging/discharging of the silicon causing the lithium and alloy reaction and the problem that a cycleability was low were not solved.

An object of the present invention is to provide the anodal active material for the novel secondary lithium battery and the secondary lithium battery which is comprised by using this.

An object of the present invention is to provide the initial efficiency, high it moreover realizes the high discharge capacity the secondary lithium battery having a cycleability and the thus used anodal active material.

An object of the present invention is to provide the anodal active material for the it solves the problem that it cannot obtain in the discharge volume and lower than the graphite system carbonaceous material a reversibility is worse than it generates the big capacity loss in a charging/discharging it is moreover incongruent for the problem, of being generated that is, the mass production it uses the silicon material containing the boron as the anodal active material for the secondary lithium battery secondary lithium battery and the secondary lithium battery which is comprised by using this.

The present invention is to provide the active material for the secondary lithium battery cathode which is comprised it resolves swelling and shrinking problem of following moreover, a charging/discharging it has the initial efficiency and the cycleability of being high it moreover

realizes the discharge capacity exceeding 372mAh / g/6 which is the theory capacity of the graphite and in which a practicality is high and the secondary lithium battery which is comprised by using this.

In order that these inventors solved the purpose, it examined in earnest the silicon material powder including the boron rather than based on the electrochemical property of the silicon material powder itself. Then, it mixed the boron of the low concentration with the silicon material powder having the proper unharvested rice crop. It could obtain the boron contain silicon material powder having in the supercooling state which did not exist from the boron amount which contained about the boridation silicon which was considerably less than amount of the presumed boridation silicon (SiB_4) of an amount the thermal process from any kind of condition as the box. It preserved the big discharge capacity which more jumped over the graphite system carbonaceous material which the silicon inherently held by using this. It found out to the capacity loss be a lot improved and exhibit the electrode characteristic of being excellent that a cycleability was excellent. The present invention is completed based on such discovery.

That is, the anodal active material for the secondary lithium battery of the present invention is made of the powder of the silicon material containing the boron. It is the thing in which the boron content is 50 weight% through 0.1 as to the silicon material.

Moreover, disclosed is 50% accumulation diameter (d_{50}) of the negative active material powder as to the desirable implementation condition of the present invention is the anodal active material which is $100 \mu m/6$ through 1. As to the other desirable implementation condition of the present invention, the anodal active material in which the ratio $I(SiB_4:021) / I(SiB_4:111)$ of the peak intensity ($SiB_4:021$) of the diffracted ray from (021) side of the SiB_4 about the peak intensity $I(Si:111)$ of the diffracted ray from the Si (111) side is 1 or less as to the X-ray wide-angle diffraction method of this negative active material powder is disclosed.

As to the present invention, and, the other sun, the boron is included or it is comprised of the compound powder of the carbon material powder, which it does not include and the silicon material powder containing the boron. The boron content discloses 50 weight% phosphorus through 0.1, and the anodal active material for the secondary lithium battery as to the boron contain silicon material powder.

It is preferable that in 50% accumulation diameter (d_{50}) of the compound powder as to the anodal active material for the secondary lithium battery about the present invention consisting of the compound powder, the to be $100 \mu m/6$. Thing through 1 is desirable the ratio $I(SiB_4:021) / I(SiB_4:111)$ of the peak intensity $I(SiB_4:021)$ of the diffracted ray from (021) side of the SiB_4 about the peak intensity $I(Si:111)$ of the diffracted ray from (111) side of Si is 1 or less as to moreover, the X-ray wide-angle diffraction method of the compound powder.

Moreover, it is preferable that the degree of crystallinity as the carbon material powder containing the boron used as to the anodal active material for the secondary lithium battery about the present invention consisting of the compound powder, or which it does not contain in other words is the high carbon material. In case the boron is materially, it is the carbon material powder which it does not do, in case of being the carbon material powder in which it contains moreover, the boron that the ratio $I(C:101) / I(C:100)$ of the peak intensity $I(C:100)$ of the diffracted ray from (100) side of the peak intensity $I(C:101)$ of the diffracted ray from (101) side of the carbon and carbon are 1 or greater, particularly it is desirable within the diffraction peak measured at the wide angle X-ray diffraction pattern of the compound powder that $I(C:101) / I(C:100)$ is 2 or greater.

The purpose is accomplished. And the present invention relates to the anodal active material as

to the secondary lithium battery, containing moreover, the anodic active material, and the anodal active material and non-aqueous electrolyte, and it is the secondary lithium battery using the silicon material powder containing the boron with 50 weight% through 0.1.

The purpose is accomplished. And the present invention relates to the anodal active material as to the secondary lithium battery, having moreover, the anodic active material, and the anodal active material and non-aqueous electrolyte, and it is the secondary lithium battery using the compound powder of the silicon material powder containing the boron with 50 weight% through 0.1 and the carbon material powder which it does not contain in other words containing the boron.

The active material for the secondary lithium battery cathode of the present invention provides the secondary lithium battery of the high energy density with a superior reversibility the capacity loss can be reduced the high discharge capacity of the silicon metal, and an oxide is preserved.

The desirable with lower part sun is given about above statement of the present invention and the other purpose, and the sun and the other advantage and it illustrates. (The above and other objects, features and advantages of the present invention will become clear from the following description of the preferred embodiments.)

■ **Structure & Operation of the Invention**

The implementation condition is given about the concrete content of the present invention and concretely it illustrates in below.

The anodal active material for the secondary lithium battery about the present invention is comprised of the powder of the thing which does to the low concentration, makes the boron to the silicon material.

This kind of boron contain silicon material powder heat-treats and the boron in the silicon material to the low concentration a mixing according to a need a crushing, and a classification and it can obtain for example. It is the boron contain silicon material powder which is in the supercooling state where amount of the silicon boride including the SiB_4 etc. is relatively small. In this way, material controlling amount of the silicon boride which produces are used as the particle size, and the specific surface area and coexisting phases. In that way the production in large quantity is possible as an electrode. In addition, it has the discharge capacity which is more greater than the graphite system carbonaceous material. And it succeeds to dramatically reduce moreover, the capacity loss in a charging/discharging and improve a cycleability.

It inquires into the effect of the boron which plays the role of being big to improve the electrode characteristic of this silicon group like a next.

If the silicon group, the silicon oxide and reaction of the lithium are based on the tin metal in which the main system and quasi-reaction are expected to be progressed, and the report (J. Electrochem. Soc., 144,6,2045 (1997)) about an oxide, it is presumed like below. That is, this reaction is elementarily, primarily regarded as the alloying · trouble alloying of the lithium and the silicon which is a host. According to the silicon is the lithium of the large amount in a charge and alloying heartburnings case, and the concentration gradient of the lithium, with causing various phase changes, the big volume expansion is generated. Reversely, in case of a discharge, as the lithium escapes from the alloy phase with the lithium, the big volume shrinkage occurs with the phase change. It is not clarified about the cause of generation of the irreversible capacity occurring in the silicon group and silicon oxide. But the form of an electrode can be collapsed in a charging/discharging due to the phase change or the big volume change occurring and it can

be caused by of the capacity loss or the reversibility degradation which is big a charging/discharging that the current collecting ratio is degraded.

By using any kind of boron contain silicon material powder that is in the supercooling state where amount of the boron compound about the present invention is relatively small it is not clarified about the reason why the irreversible capacity reduces. But when it compares with for example, the silicon group, the charge depth is shallow and the expansion of the crystalline structure is suppressed in the case where the maximum alloy composition with the lithium of the boron contain silicon material powder of the present invention is less. Therefore, the degradation of the current collecting ratio is held back and the irreversible capacity reduces. But in case it becomes the crystalline structure which is suitable for the diffusion of the lithium by containing the boron, the diffusion of the lithium is more speeded up and since the electric conductance of the material itself is improved, it thinks as the thing which the irreversible capacity reduces, and the formation of the acceptor level by the doping of the boron on the pure silicon that the irreversible capacity reduces.

It has the form of the material including the boron in the silicon to the powdered having the unharvested rice crop of the proper extent. By using this for the anodal active material of the secondary lithium battery the graphite system carbonaceous powder which recently is put to practical use is mounted, or the electrode manufacture line of the lithium ion battery can not be changed and it can use. Therefore, the mass production of the battery at the existing facility is possible. Moreover, since the polarization resistance under the big electric current density in which the thinning which is advantageous for the diffusion of the lithium within an electrode is possible and is low suppressed, the quantity of electricity efficiency in a charging/discharging is improved and when powder is compared with the conventional alloy structure in the electrode coating and forms, the capacity loss can be reduced.

It experiences about the boron contain silicon material powder about the present invention and it need to be satisfied 50% through 0.1 as to the silicon material powder as the boron concentration with the weight conversion. Since it enough does not display an effect and in case the boron concentration is 0.1 weight% less than, the boron is contained the big capacity loss is shown in the same charging/discharging as the silicon group, it is not desirable. In the meantime, as the boron concentration contained the boron to a material more than 0.1 weight%, the dramatic improvement of the electrode characteristic was shown. Moreover, in case the boron concentration exceeds 50 weight%, the silicon boride including the SiB_4 etc. does not contribute to the occulsion (alloying) reaction of the lithium. Therefore, generated to the large amount the per weight discharge capacity, and the energy density are extremely degraded. Therefore, it is not desirable. More preferably, it is desirable that the boron concentration is 10 weight% or 50 weight%. Is more desirable. What is 20 weight% or 40 weight%. If it becomes the boron amount content included among the silicon material powder over 10 weight%, the cycleability higher than the silicon material powder is shown. As to this, in case the boron content is low as to the phenomenon that swelling and shrinking of the silicon material powder accompanied among the review of the present invention with a charging/discharging by the discovered boron addition are suppressed, the effect is decreased, it is regarded.

Moreover, it is preferable that more preferably, 50% accumulation diameter (d_{50}) of the powder about the unharvested rice crop of the boron contain silicon material powder about the present invention is satisfied $50 \mu\text{m}/6$ through 5 with $100 \mu\text{m}/6$ through 1. Since it has the tendency that it is very much necessary to have the thing, in which the tendency that the handling property is deteriorated since the pulverized body of the small grain size is very much included in case of being d_{50} this 1 {TSRS is recognized and binder or the conductive agent and the energy density per unit volume is degraded, it is not desirable. In the meantime, in case of exceeding the d_{50}

this $100 \mu\text{m}/6$, it has possibility to get into difficulty that the lithium is diffused to the inside of the active substance powder. But since it is difficult for the electrode preparation in which the electrode thickness of the existing lithium ion battery is an extent less than $200 \mu\text{m}/6$, it is not desirable.

It is preferable that the particle size specific surface area of the boron contain silicon material powder is $100\text{m}^2/\text{g}$ or less. In case this specific surface area exceeds $100\text{m}^2/\text{g}$, since the surface area is big, the reaction with an electrolyte is produced in the initial charge and the capacity loss is enlarged. But it occludes in the rechargeable cycle among material, or since the reactivity of the solvent of the middle transmitted with the lithium becomes higher and the safety is possible to be lowered, it is not desirable. In the meantime, is not limited specially as the lower limit of the specific surface area. But it is difficult that the lithium is diffused to the inside of the active material powder. But it therefore does to about $0.01\text{m}^2/\text{g}$ with possibility. That it is difficult for the thin electrode preparation.

Moreover, the diffracted ray each peak intensity $I(\text{Si}:111) / I(\text{SiB}_4:021)$, from (021) side of the diffracted ray from the side of the Si (111) within the diffraction peak, observed as to the present invention to the wide angle X-ray diffraction pattern measurement of the boron contain silicon material powder and SiB_4 is $I(\text{SiB}_4:021) / I(\text{Si}:111) \leq 1$

It is preferable that it is satisfied the relationship which becomes.

It means that the SiB_4 coexisting exists among material with large amount in case this peak intensity ratio exceeds 1. The SiB_4 itself contributes to the occlusion (alloying) reaction of the lithium. Therefore, the per weight discharge capacity, and the energy density are extremely degraded. It is due to have the concern which a cycleability is decreased.

At this time, the wide angle X-ray diffraction pattern of the silicon material powder derived from containing the boron among the active material for the lithium ion secondary battery of the present invention is mainly returned to the peak of the SiB_4 derived from and Si. But the silicon material powder containing the boron is not simple mixture of the SiB_4 and the simple Si. It is recognized as an observation by the transmission electron microscope in the thing in which the minute boridation silicon (SiB_4) is segregated among each particle of the silicon material powder containing the boron with multiple or the thing, having in the precipitation initial step moreover, each particle of the silicon material powder that it very much exists to be twisted with local considerably complicated. The detailed mechanism is not clear. But it is twisted with the boron or the local, many employed among the size of this kind of the precipitation SiB_4 or the eduction form or the silicon material powder an etc. contributes to the excellent performance expression of the active material of the present invention and it thinks these inventors.

Moreover, the existence ratio of the SiB_4 which the peak intensity ratio means is determined as the boron amount and the reaction temperature (as to the common way (相??) of the silicon and boron, it is reported in the J. Less-Common Met., and 71,195 (1980) for example) adding to the balance lawn. But amount of the silicon boride including the SiB_4 etc. depends on the silicon form or the firing pattern which is the raw material among a material. Coexists. Particularly, it is possible that the silicon which is the raw material is the powder. In case the drop temperature process at the thermal process is fast, therefore the existence ratio of the SiB_4 among a material dispenses the boron contain silicon material having in the supercooling state in which amount of the silicon boride is relatively small with discoloration.

Moreover, that is, the boron contain silicon material powder about the present invention a price can be included under the reason for illustrating in below to it specially does not limit about the boron contain silicon material powder about the present invention as the lower limit of the peak

intensity ratio I (SiB₄:021) / I (SiB₄:111) exhibits the dramatic enhancement as to the electrode characteristic. The boron is perfect as to the sun adding the small amount in this way, it employs with the silicon, and the peak of the SiB₄ is observed compared to case, as described above, it is the silicon material singleness with a small amount of boron contain called 0.1 weight%. Moreover, presently, occasionally, as to the precision of measurement of the wide angle X-ray diffraction, it experiences and the detection threshold value of the peak intensity ratio is about 0.01. It is difficult to determine as the noise in the back ground even if the diffraction peak derived with the SiB₄ exists than this as to the low value. For this reason, in case it experiences and the peak intensity ratio is 0.01 or less, it is difficult to clearly determine whether or not. But whether the diffraction peak of the SiB₄ derived from existed or not it is, or it is evident that the boron is contained among the silicon material particle. It has in the state that the boron is perfect, is employed in the silicon, or it separately does in other words that a part is segregated as the silicon boride. And yet, the embodiment of the present invention is. Moreover, the peak intensity ratio as to the case, of being 1 or less is included in the present invention over 0.01 as the desirable embodiment.

Moreover, it is not specially prescribed about the degree of crystallinity of the silicon material powder containing the boron. But in case the degree of crystallinity of the silicon material powder containing the boron is lower than an extremity, it is not desirable in (the determinant size evaluated in the X-ray diffraction is 10nm or less for example) in the point of view of doing as the secure of the stabilized voltage which does not depend on the amount of discharge of the case of the electric potential nots showing the dependability which is uniform about amount of charge and discharge (flat) and being used in the charging/discharging for a battery.

It is not limited specially. But it can be manufactured with for example or less, an invention. That is, after it raises temperature to 1350°C or 1400°C about the silicon powder of 100 μm/6 through the d₅₀ this 1 under the argon atmosphere to mix the boron compound powder of 50 weight% through 0.1 to the boron conversion, it preserves with 10 hour through 1. After it cools quickly to 600°C at the speed of the extent which thereafter pays with 15°C /, it cools to the speed of the extent paying with 5°C / to the near room temperature. According to a need, the powder obtained with the plasticity regulates the unharvested rice crop with a pulverizing, and a classification. The sintering atmosphere at this time is the non-oxide atmosphere. It is possible to use the nitrogen etc. besides for example, the argon.

At this time, it may be acceptable that the silicon powder used as raw material includes various elements besides Si. For example, the carbon, the oxygen, the hydrogen, the nitrogen, the sulfur, the phosphorus, the halogen, the alkali metal, the alkaline earth metal, the transition metal, al. ga, in, ge, sn, pb, sb, bi etc are contained at least. As to the total content of this element, 10 weight% through 0 is desirable. Moreover, 5 weight% through 0 is more desirable.

Moreover, and, it is possible that finally the boron compound powder which is one raw material can employ as the boron concentration within the provision range of the present invention among the silicon in the form of the boron. It is the boron compound. It appropriately uses for example, one kind among the boron group, the oxidation boron, the boric acid, the boron carbide, the boron nitride or the plurality.

It becomes about the method of mixture if it is enough uniformly mixed with a sample. For example, for example, the V- blender, the kneader, the ball mill etc. can be appropriately used. But it is not specially thus restricted. Moreover, in the particle size of the boron contain silicon material powder after the plasticity, and the control of the specific surface area, the method for being commonly used can be used. For example, in the ball mill, the pin mill, the disc mill, the impeller mill, the jet mill, the roller mill, the stamp mill, the cutting mill etc is a classification, the air classifier, etc. are appropriately used. But it is not specially thus restricted.

Moreover, it is possible that the anodal active material for the secondary lithium battery about the present invention more adds the carbon material powder in the boron contain silicon material powder as described above and it is done by such compound powder.

That is, the sun is the thing which is the compound powder with the powder of the silicon material containing the boron of 50 weight% through the carbon material powder and 0.1 in desirable one room of the anodal active material for the secondary lithium battery of the present invention.

In case it is done by this kind of compound powder, the anodal active material about the present invention has the high discharge capacity. In spite of that it have the specially excellent performance about the expansion shrinkage in a cycleability and charging/discharging. The reason was not clarified. But the carbon material powder of the high degree of graphitization is remarkably contained among the compound powder with the carbonic acid material powder. Generally this kind of carbon material powder is readily transformable. Therefore it is regarded as one of the important reason to buff relatively big swelling and shrinking which are accompanied with the charging/discharging of the silicon material powder containing the boron.

In the present invention, the used carbonic acid material powder becomes even if it materially does not contain the boron. It contains the boron.

At this time, is desirable in the point of view of the discharge capacity what is the carbon material powder which has as the carbon material powder (what is called, the high degree of graphitization) that the degree of crystallinity is high. The high degree of crystallinity can confirm with the X-ray diffraction etc. In this case, the carbon material powder functions as the anodal active material which has the discharge capacity of about 300mAh / g/6 with functioning as the conductive material.

It is preferable that 50% accumulation diameter (d_{50}) of the powder like the case, where the anodal active material about the present invention comprises anodal active material the boron as described above as to the sun which is the compound powder between the carbon material powder and the boron contain silicon material powder about the particle size with the containing silicon material powder in this way is satisfied $100 \mu m/6$ through 1. Moreover, it is preferable that it is $100m^2/g$ or less about the specific surface area of the boron contain silicon material powder like above statement.

In the meantime, it is preferable that a constellation as the pulverized body including the distribution of the average particle diameter, the particle size distribution, the specific surface area, the tap density, the powder particle, the particle shape of the carbon material powder and angle of repose etc. it is satisfied a constellation as the required pulverized body with the active material for the secondary lithium battery cathode a constellation as the pulverized body of the active material for the secondary lithium battery cathode is nearly determined with a constellation as the pulverized body of the carbon material powder is manufactured. For example, it is preferable that in the thing which the average particle diameter of the carbon material powder is .50 {TSRS over $10 \mu m/6$, the specific surface area is $5m^2/g$ or less over $0.1m^2/g$.

The carbon material powder among the active material for the secondary lithium battery cathode of the present invention can be manufactured with the method of below for example. Firstly, in case of the carbon material powder which does not contain the boron, the coal tar group pinch cokes (the carbonization bosom) is and distributes crushed. The carbon material powder which dispenses so that for a particle less than $10 \mu m/6$, 10% or less be to 325 mesh less than to a volume and is obtained is preserved to the non-oxide atmosphere about $2900^\circ C$ including the

argon atmosphere etc. after the increase in temperature with White heat hour. Thereafter it cooling-emits to the near room temperature. The powder obtained with the thermal process obtains the carbon material powder possible to be used with the simple pulverizing for the active material for the secondary lithium battery cathode of the present invention. Moreover, in case of the carbon material powder containing the boron, the cor tar group pinch cokes (the carbonization bosom) is and distributes crushed. After adding and mixing one kind of the boron unit, the oxidation boron, the boric acid, the boron carbide, the boron nitride etc less than 325mesh or a plurality of boron compound powders about the carbon material powder which it dispenses so that for a particle less than $10 \mu m/6$, 10% or less be to 325mesh less than to a volume and it can obtain to the boron conversion with about 0.5wt% or about 10wt%, it raises temperature to the argon atmosphere about $2900^{\circ}C$, it preserves with White heat hour. Thereafter it cooling-emits to the near room temperature. In this case, generally, this is performed since the crushing · classification of a post-baking is needed. The carbon material powder can use only in the active material for the secondary lithium battery cathode of the present invention is obtained.

In case anodal active material used for the secondary lithium battery of the present invention are the mixture between the carbon material powder and the boron contain silicon material powder, the carbon material powder is not limited specially. And as described above, the artificial graphite of the petroleum tar derived from, the natural graphite, the Kish graphite etc. can be obtained besides the artificial graphite of the cor tar derived from. It moreover can use for these as the thermal process etc. to include the boron rather than.

Thing satisfying the specific condition the active material for a cathode presents to below about the sun which is the compound powder between the carbon material powder and the boron contain silicon material powder in this way about the present invention are more desirable.

That is, a mixing , and the compound powder which is obtained by compounding, are based the silicon material powder having the boron content and the proper crystallographic feature of the proper extent upon the carbon material powder having the proper crystallographic constellation to the rate which is appropriate according to the boron content among the silicon material powder on the discovery of these inventors that the problem of swelling and shrinking which the condition presented to below accompanies in the charging/discharging realizing the discharge capacity exceeding $372mAh / g/6$ which is the theory capacity of the graphite and has the moreover high initial efficiency and the cycleability of being high is minimally supressed.

Moreover, in case the used carbon material powder materially does not contain the boron to the first, the carbon content among the compound powder the x (wt%), and the silicon content the y (wt%), and the boron content is done to the z (wt%). A $x+y+z$ is materially called 100%

It is possible that the compound powder makes into high capacity by being satisfied $0.01+0.1 \times z / (y+z) \leq (y+z) / (x+y+z) \leq 0.15 + z / (y+z)$ (1). It has the stem cured efficiency, and the high cycleability. Swelling and shrinking in a charging/discharging are suppressed. A thing satisfying $0.05+0.1 \times z / (y+z) \leq (y+z) / (x+y+z) \leq 0.1 + z / (y+z)$ is more desirable. In case $(y+z) / (x+y+z)$ is smaller than $0.01+0.1 \times z / (y+z)$, the concern which cannot obtain enough discharge capacity has the compound powder. Moreover, the discharge capacity of the compound powder is big when $(y+z) / (x+y+z)$ is greater than $0.15 + z / (y+z)$. But swelling and shrinking of a cathode by a charging/discharging are enlarged. Therefore, it has the concern which cannot realize the cycleability that the compound powder is sufficient.

Secondly, in case the carbon material powder contains the boron, it has the content of the boron existing as the z 2 (wt%) and $z=z1+z2$ among the carbon material powder containing the z1 (wt%), and the boron the content of the boron existing among the silicon material powder

containing the y (wt%), and the boron the x (wt%), and the silicon content the carbon content among the compound powder. A $x+y+z$ materially does as 100%

The compound powder makes into high capacity by being satisfied $0.01+0.1\times zl / (y+zl) \leq (y+zl) / (x+y+z) \leq 0.15 + zl / (y+zl)$ (2). It has the high initial efficiency, and the high cycleability. Swelling and shrinking in a charging/discharging are suppressed. The thing satisfying $0.05+0.1\times zl / (y+zl) \leq (y+zl) / (x+y+z) \leq 0.1 + z / (y+zl)$ is more desirable. ($y+zl$) In case the $z / (x+y+z)$ is smaller than $0.01+0.1\times zl / (y+zl)$, the concern which cannot obtain enough discharge capacity has the compound powder. Moreover, the discharge capacity of the compound powder is big when $(y+zl) / (x+y+z)$ is greater than $0.15 + zl / (y+zl)$. But swelling and shrinking of a cathode are enlarged with a charging/discharging. The concern which cannot realize the cycleability of being sufficient has the compound powder.

It is preferable that in case the compound powder of the silicon material powder containing the boron and the carbon material powder which it does not do the boron is materially is satisfied the condition (1), the compound powder between the carbon material powder containing the boron and the silicon material powder containing the boron are satisfied the condition (2) in other words. In that case, it describes in the above about the boron content which is desirable as to the silicon material powder containing the boron. As described above, the ratio $I(SiB_4 : 021) / I(SiB_4 : 111)$ of each peak intensity of the diffracted ray from (111) side of the diffracted ray from (021) side of the SiB_4 and Si are 1 or less within the diffraction peak observed to moreover, the wide angle X-ray diffraction pattern measurement of this compound powder.

Moreover, it is preferable that in case the compound powder between the carbon material powder which it does not do the boron is materially and the silicon material powder containing the boron are satisfied the condition (1), the diffracted ray of 2 within the carbon material powder derived from, that is, each peak intensity $I(C: 101)$ of the diffracted ray from (100) side of the diffracted ray from (101) side of the carbon and carbon and $I(C: 100)$ are satisfied $I(C: 101) / I(C: 100) \geq 1$ within the diffraction peak measured at the wide angle X-ray diffraction pattern about the carbon material powder. At this time, the discharge capacity is enlarged because the degree of crystallinity (the degree of graphitization) of the carbon material powder oneself is high. Therefore, the amount of mixing of the silicon material powder containing the boron can be lowered. Consequently the expansion ratio by the charge of the cathode material whole is low suppressed.

There is a problem that in case the peak intensity ratio $I(C: 101) / I(C: 100)$ is less than 1, the discharge capacity of the carbon material powder oneself becomes smaller. The need to mix the silicon material powder which contains the boron in order to realize the discharge capacity exceeding the theory capacity of the graphite to the large amount is generated. The expansion ratio is enlarged with a charge as the cathode material. Therefore, it becomes difficult to exhibit the cycleability that the compound powder is sufficient.

Moreover, in case the compound powder with the silicon material powder containing the carbon material powder and the boron containing the boron is satisfied the condition (2), the degree of crystallinity of the carbon material powder generally containing the boron is high. The discharge capacity is large. Therefore, it is desirable that the carbon material powder originally contains the boron. Particularly, it is preferable that the weight proportion of the boron contained among the carbon material powder about the carbon material powder middle is 10% or less over 0.5%. As been evident, the crystallization of the carbon material powder nearly does not contribute to an improvement through the wide angle X-ray diffraction pattern measurement and it produces $B_4C/6$ which is an inactive to an electrochemical. It becomes the result the content of the boron more than 10% does not contribute to the capacity enhancement at all, of reducing the capacity per weight as the minute creating with $B_4C/6$. Moreover, it is preferable that each peak intensity

$I(C: 101)$ of the diffracted ray from (100) side of the diffracted ray from (101) side of the carbon within the diffraction peak, which the carbon material powder containing the boron is measured at the wide angle X-ray diffraction pattern and carbon and $I(C: 100)$ are satisfied $I(C: 101) / I(C: 100) \geq 2$. At this time, the degree of crystallinity of the carbon material powder is more improved. Therefore, it becomes easy to reveal the capacity in which it is near the theory capacity of the graphite.

As to the sun in which the active material for the secondary lithium battery cathode of the present invention contains the boron or which is the compound powder of the silicon material powder containing the boron and the carbon material powder which does not contain, the most of silicon and carbon materially does not mix in the atomic level which chemically does not form the compound or the solid solution. But it does not have the need to be certainly the simple mixing of the powder of this 2 kind. While pulverizing by using for example, the special pulverizing device in the range that remarkably does not obstruct the functional effect of the present invention, the range mixes. Moreover, it may be acceptable that a part chemical alloying is proceeded. It consists of the form which moreover, the powder of this cranium partially, partly sticks.

It becomes about the method of mixture of the boron contain silicon material powder and carbon material powder if it is enough uniformly mixed with the powder. For example, the powder of this 2 kind is mixed by appropriately using V blender, a kneader, the ball mill etc., or it wet can mix. But it is not specially restricted to this kind of method of mixture. Moreover, it may be acceptable that the characteristic of being excellent of the boron contain silicon material powder is not influenced. The fractional response or the fusion of a particle occurs in the mixing process. Moreover, it is possible that in a control including the particle size of the carbon material powder, containing the boron of a post-bake the specific surface area etc., the method for being used ordinarily is used. For example, in a crushing, the air classifier, etc. of the ball mill, and a ball, the disc mill, the impeller mill, the jet mill, the roller mill, the stamp mill, the cutting mill etc spreading are appropriately used to a classification. But it is not specially confined to these.

But it is preferable that preferably the point, that the weight of the standard anodal active material used for the miniature lithium ion secondary battery 1 which is less by about 10g and coating thickness the mixing process can achieve the marked uniformity less than about 100 {TSRS due to the thin spot the weight of the standard anodal active material used for the miniature lithium ion secondary battery 1 which is the mixing at the level of the powder particle each. After this marked uniformity charges the cathode amount active material 1 parts by weight the water which small amount mixes a surfactant or the isopropyl alcohol or the methanol or the ethanol etc. about 2 parts by weight for example, after so called performing the wet mixing, by pulverizing it can get a drying. But it is not specially restricted to this method.

The dispensing of the active material for the secondary lithium battery cathode of the present invention was illustratively illustrated. But the active material for the secondary lithium battery cathode of the present invention is not restricted by a dispensing. The example of the other control method of the active material for the secondary lithium battery cathode of the present invention does the Ar gas to the carrier gas and it processes with plasma the mixing gas of the specific ratio of the silane gas and diborane gas and it obtains the boron contain silicon material powder. It obtains the silicon material powder which contains the usable boron in the active material for the secondary lithium battery cathode of the present invention by heat-treating this in about 1380°C with White heat hour. By highly equality-mixing the carbon material powder containing this and carbon material powder or the boron the active material for the secondary lithium battery cathode of the present invention obtains. In the other example, by using the mill mixing the silicon powder and boron metal to the specific ratio, it allows about 20 hours 10

minute mechanical. It heat-treats in about 1380°C with White heat hour to be obtained. The silicon material powder containing the usable boron in the secondary lithium battery anodal active material of the invention performing the crushing classification of the appropriate an extent is obtained. By highly equality-mixing the carbon material powder containing this and carbon material powder or the boron the active material for the secondary lithium battery cathode of the present invention is obtained.

The active material for the secondary lithium battery cathode of the present invention is materially comprised of the boron and silicon or the carbon and boron and silicon. But it is the range that remarkably does not obstruct the functional effect of the present invention. If it is the case, it contains the other element as the impurity of the technical level derived in the raw material or the manufacturing process or the apparatus or the other element inevitably introduced with the operation condition. The range adds the other element or the compound to any kind of purpose.

The performance of the active material for the secondary lithium battery cathode of the present invention is adequately taken out as the method for building up a cathode by using the active material for the secondary lithium battery cathode of the present invention. Moreover, parents and brothers nature are high. The performance is not thus limited at all if it is electrochemically stabilized. After the conductive agent, a polytetrafluoroethylene, including, the powder or the dispersion solution of the fluorine-based resin including the carbon black etc. is added in the example lower-part, and the silicon material powder, it has a mixing, and the method for mixing. Moreover, after the conductive agent and polyethylene, the resin powder of the polyvinyl alcohol lamp including the carbon black etc. are added in the silicon material powder, the dry mix is inserted into the mold and it has the method for molding with the hot press. Moreover, it has the conductive agent, the polyvinylidene fluoride (PVdF), including, the fluorine side resin powder or the carboxymethylcellulose, including, the water soluble adhesive including the carbon black etc. as a binder in the silicon material powder. By mixing by using the N-methylpyrrolidone (NMP), the dimethylformamide or the water, and the solvent of the alcohol lamp the slurry is prepared. It can mold on the current collector with coating by being dry.

Moreover, as to the sun in which the active material for the lithium ion secondary battery cathode of the present invention is the compound powder between the carbon material powder and the boron contain material powder, the carbon material powder coexisting or the carbon material powder containing the boron enough exhibits a function as the conductive material. Therefore, a cathode is built up. It does not have the need to specially add the conductive material including the carbon black etc.

The anodal active material of the present invention appropriately assembles with the anodic active material and non-aqueous electrolyte (for example, the organic solvent system electrolyte) and it can use. But these non-aqueous electrolyte (for example, the organic solvent system electrolyte) or the anodic active material specially does not limit this if it can be commonly used in the secondary lithium battery.

The Chevrel phase compound or the activated charcoal, indicated as for example, for example, the lithium-containing transition metal oxide $\text{LiM (1)}_x \text{O}_2$ (among an equation, a x is the value of the range of $0 \leq x \leq 1$. M (1) shows the transition metal among an equation. It is comprised of one kind among the co, ni, mn, cr, ti, V, fe, zn, al, in, sn at least) or $\text{LiM (1)}_y \text{M (2)}_{2-y} \text{O}_4$ (among an equation, a y is comprised of M (1) among an equation it is the value of the range of $0 \leq y \leq 1$. and one kind M (2) shows the transition metal), the transition metal chalcogen cargo (the TiS_2 , NbSe_3 etc), the vanadium oxide (V_2O_5 , V_6O_{13} , V_2O_4 , V_3O_8 etc) and Li compound, and general equation $\text{M}_x \text{Mo}_6 \text{Ch}_{8-y}$ (among an equation, a x $0 \leq x \leq 4$, and a y are the value of the range of $0 \leq y \leq 1$. M a metal including the transition metal, and Ch shows the

chalcogen element among an equation) as the anodic active material the active carbon fiber etc. can be used.

As to the non-aqueous electrolyte (for example, the organic solvent system electrolyte), is not limited specially as the organic solvent. But for example, the mixed solvent more than the singleness of the polypropylene carbonate, ethylene carbonate, butylene carbonate, chloroethylene carbonate, dimethyl carbonate, diethyl carbonate, 1, 1-dimethoxyethane, 1, 2-dimethoxyethane, 1, 2-diethoxyethane, γ -butyrolactone, tetrahydrofuran, 2-methyltetrahydrofuran, 1, 3-dioxolane, 4-methyl-1, 3-dioxolane, anisole, diethylether, sulfolane, methyl sulfolane, acetonitrile, chloronitrile, propionitrile, boronic acid trimethyl, silicic acid tetramethyl, nitromethane, dimethylformamide, N-methylpyrrolidone, ethyl acetate, trimethylol carelessness mate, nitrobenzene, benzoyl chloride, embrittled benzoyl, tetrahydrothiophene, dimethyl sulfoxide, 3-methyl-2-oxazolidone, ethylene glycol, sulfite, a dimethylsulfite etc or 2 kind can be used.

The publicly known thing can be used from a convention as an electrolyte as nothing. For example, a mixture more than one kind of the LiClO₄, LiBF₄, LiPF₆, the LiAsF₆, LiB(C₆H₅), LiCl, LiBr, the LiCF₃SO₃, LiCH₃SO₃, Li(CF₃SO₂)₂N/6, the Li(CF₃SO₂)₃C/6, the Li(CF₃CH₂OSO₂)₂N/6, the Li(CF₃CF₂CH₂OSO₂)₂N/6, the Li(HCF₂CF₂CH₂OSO₂)₂N/6, the Li((CF₃)₂CHOSO₂)₂N/6, the LiB[C₆H₃]₄ etc or 2 kind can be given.

The expression method and method of measurement of the different property used in the rules of the anodal active material for the secondary lithium battery of the present invention are disclosed in below.

(1) The carbon content, the silicon content, and the boron content.

It was the fixed quantity with the ICP method (inductively coupled high frequency plasma spectroscopy).

(2) 50% accumulation diameter(d₅₀)

By computing the diffraction pattern when irradiating the parallel rays in the dispersed particle the particle size distribution was interpreted (plan saturation diffraction). It had the grain size when for the weight accumulation, 50% was as 50% accumulation diameter (d₅₀) and it saved. An ordinarily, and each sampling medicine 0.2g were put into the water 20cc as the dispersing medium. By using to add the surfactant which subsequently came into the market with 3 drop through 2, it measured with the Seishin enterprise the particle size apparatus for measuring dispersion LMS-24.

(3) Specific surface area.

By interpreting by using the BET law based on the adsorption quantity curve about each nitrogen partial pressure when absorbing the nitrogen in a sample the specific surface area was saved. It measured with the Japanese bell corporation the BELSORP-36 by using an ordinarily, and 2g through each sample 1.

(4) I(SiB₄:021) / I(Si:111)

X rays of a monochrome is cremated to the collimated beam. It irradiates in the sample powder and (111) of Si the peak and corresponding to (021) side of the SiB₄ is measured. The peak intensity ratio I(SiB₄:021) / I(Si:111) was produced from the back ground each peak intensity.

(5) I(C:101) / I(C:100)

X rays of a monochrome is cremented to the collimated beam and it irradiates in the sample powder and each peak of the diffracted ray from the side of the diffracted ray from (101) side of the carbon and carbon (100) are measured. The peak intensity ratio I (C:101) / I (C:100) was produced from the back ground each peak intensity.

[Embodiment]

The concrete embodiment of the present invention is given in below. More concretely, the present invention is illustrated. But the embodiment illustrated in below is done by a purpose to more specifically make the content of the present invention understand. It is ever not to limit the present invention.

Embodiment 1.

After the boron powder (purity 99.9%) being added in silicon powder (the purity 99.9%, and the $d_{50} = 10 \mu\text{m}/6$) to the weight conversion with 1% and using a kneader, it enough mixed, this mixture was raised temperature to 1400°C among the argon air current. It preserved at the ionic degree with 5 hour. The silicon material powder for the secondary lithium battery cathode was obtained by cooling to the room temperature with about 3 hour. In this way, the boron amount included in the silicon material powder manufactured was 0.5% to the weight ratio. After the obtained boron contain silicon material powder was pulverized with the impeller mill, a mouth controlled by using the air classifier. In that way the powder in which 50% accumulation diameter (d_{50}) was 15 $\mu\text{m}/6$ was obtained. The specific surface area of this powder was $5.1\text{m}^2/\text{g}$. This material was and measures diffracted X rays. Then, the peak of the SiB_4 was not observed and 0 became the peak intensity ratio I (SiB_4 :021) / I (Si:111). The boron among a material was altogether employed with the silicon.

The carbon black the polytetrafluoroethylene powder was added about this boron contain silicon material powder 70 weight% as the conductive agent as 20 weight%, and a binder with 10 weight% and it mixed. The electrode sheet of about 0.1mm thickness was prepared. 1cm each (about 21mg with the weight) was cut away (about 15mg it converts into the silicon material). By compressing in the Cu mesh which was the current collector the cathode electrode was prepared.

In order that the electrode characteristic at the unipolar of the molding electrode was evaluated. 3 pole equation cell using the lithium metal in the Euphorbiae pekinensis Radix, and the reference pole was used. It used as an electrolyte to dissolve the LiPF_6 at the mixed solvent (volume ratio 1:1 mixing) of the diethyl carbonate and ethylene carbonate to the rate of 1mol /1. It altogether performed about the rechargeable test under the electric potential regulation to the constant current ($0.5\text{mA}/\text{cm}^2$) with a charge, and a discharge. The potential window did from 0V to 2.0 V (lithium metal standards). It evaluated as this kind of a condition. Then, 2500mAh / g/6, and the initial discharge capacity this boron contain silicon material powder of the initial charging capacity the initial capacity loss was small to 2000mAh / g/6 to 500mAh / g/6. The capacity loss was not nearly seen after 2 time. Moreover, as to the discharge of 2 times next, without nearly changing, the discharge capacity showed the cycleability of being excellent. It had the considerably high electrode efficiency.

Embodiment 2.

In the extrinsic adding the boron to the weight conversion with 10%, a material was dispensed to the embodiment 1 and similar condition. The boron amount included among the obtained

material was 9.0% to the weight ratio. After the obtained boron contain silicon material powder was pulverized with the jet mill, a mouth controlled by using the air classifier. In that way the powder in which 50% accumulation diameter (d_{50}) was $20 \mu\text{m}/6$ was obtained. The specific surface area of this powder was $3.5\text{m}^2/\text{g}$. This material is and measures diffracted X rays. Then, the considerably small peak corresponding to the SiB_4 is observed with the peak corresponding to the silicon. 0.05 becomes the peak intensity ratio $I(\text{SiB}_4:021) / I(\text{Si}:111)$. The boron among a material is altogether employed with the silicon.

In this way, the boron contain silicon material powder dispensed was evaluated as the same condition as the embodiment 1 with electrode. Consequently, as to this boron contain silicon material powder, $2400\text{mAh} / \text{g}/6$, and the initial discharge capacity of the initial charging capacity the initial capacity loss was small to $2000\text{mAh} / \text{g}/6$ to $400\text{mAh} / \text{g}/6$. The capacity loss was not nearly seen after 2 time. Moreover, as to the charging/discharging of 2 times next, the discharge capacity has the electrode characteristic of being considerably high showing the cycleability of being excellent without nearly changing, etc.

Embodiment 3.

In the extrinsic adding the boron to the weight conversion with 50%, material were dispensed to the same condition as the embodiment 1. The boron amount contained among obtained material was 48.9% to the weight ratio. After the obtained boron contain silicon material powder was pulverized with the pin mill, a mouth controlled by using the air classifier. In that way the powder in which 50% accumulation diameter (d_{50}) was $5 \mu\text{m}/6$ was obtained. The specific surface area of this powder was $25.3\text{m}^2/\text{g}$. Moreover, this material was and measures diffracted X rays. Then, the peak corresponding to the SiB_4 was observed with the peak corresponding to the silicon. 0.88 became the peak intensity ratio $I(\text{SiB}_4:021) / I(\text{Si}:111)$. A part of the boron was employed with the silicon and a part SiB_4 was generated.

In this way, the boron contain silicon material powder dispensed the electrode evaluation was performed to the same condition as the embodiment 1. Consequently, as to this boron contain silicon material powder, $800\text{mAh} / \text{g}/6$, and the initial discharge capacity of the initial charging capacity the initial quantity loss was less by $500\text{mAh} / \text{g}/6$ by $300\text{mAh} / \text{g}/6$. The capacity loss was not nearly seen after 2 time. Moreover, as to the charging/discharging of 2 times next, without nearly changing, the discharge capacity shows the cycleability of being excellent. It has the considerably high electrode efficiency.

Comparative Example 1.

The silicon powder (purity 99.9%) was used as the anodal active material for the secondary lithium battery. 50% accumulation diameter (d_{50}) of this powder was $10 \mu\text{m}/6$. The compare dimension was $8.7\text{m}^2/\text{g}$. This material the electrode evaluation was performed to the same condition as the embodiment 1. Consequently, as to this anodal active material, the initial discharge capacity was large with $2000\text{mAh} / \text{g}/6$. But the initial charging capacity was $3300\text{mAh} / \text{g}/6$ and the initial quantity loss was considerably serious with $1300\text{mAh} / \text{g}/6$. The capacity loss is large in 2 times with the repetition of the continuous charging/discharging with $800\text{mAh} / \text{g}/6$. Thereafter it is gradually degraded and $0\text{mAh} / \text{g}/6$ barely in 7 time. For this reason, the total capacity loss was considerably big. Moreover, the discharge capacity was drastically degraded and the discharge capacity fell down to 10 time with the progressing of a cycle to $200\text{mAh} / \text{g}/6$. It could not utilize as the secondary lithium battery dragon.

It dispensed in the extrinsic adding the boron to the weight conversion with 56% to the same condition as the embodiment 1 of a material. Moreover, the obtained boridation silicon material powder was pulverized with the impeller miller. In that way 50% accumulation diameter (d_{50})

obtained the powder of $20 \mu\text{m}/6$. The specific surface area of this powder was $2.1\text{m}^2/\text{g}$. The boron amount included among the obtained material was 54.5% to the weight ratio. Moreover, this material is and measures diffracted X rays. Then, the peak corresponding to the SiB_4 / SiB_6 is observed with the peak corresponding to the silicon. The peak intensity ratio $I(\text{SiB}_4:021) / I(\text{Si}:111)$ is to 0.96. The solid solution sieve's of the boron – silicon employing the boron as the high concentration is generated. Simultaneously, it is generated and the boron exceeding a high-capacity coexists the SiBS_4 . The silicon boride (SiB_6) of the higher boron concentration is generated with the little amount.

In this way, the boron contain silicon material powder dispensed the electrode evaluation was performed to the same condition as the embodiment 1. Consequently, as to this boron contain silicon material powder, the initial charging capacity was low suppressed by $370\text{mAh/g}/6$. Since it added in the SiB_4 and the silicon boride (SiB_6) of the high concentration more coexisted, the initial discharge capacity was considerably relatively small by $170\text{mAh/g}/6$. Moreover, using the repetition of a charging/discharging, the discharge capacity was more degraded after 2 times and $140\text{mAh/g}/6$ was in 10 time. It could not utilize as the secondary lithium battery.

6 through the embodiments 4 through 10 and comparative example 3.

<The preparation of the material powder>

After using the ball mill, the pitch coke powder obtained from the cor tar pitch was pulverized, a sieve was hit with 325mesh. It took out to a sieve to drop. Boron powder (the purity 99.9%, and 325mesh less than) the amount of addition were diversified and it sealed in this among the graphite geno of a cylindrical (4 kind of 0, 2, 4, 6 wt% with the boron concentration) to well mix. It shut tightly to the lid in which a screw stuck.

This seal scull was raised temperature to 2900°C at the ramp-up rate of about $12^\circ\text{C}/\text{min}$ with the electric furnace while passing away the Ar gas $10\text{L}/\text{min}$. It temperature-decreased to the room temperature after preserving in the ionic degree with 1 hour. By using the impeller mill, the carbon-powder taken out of the graphite container of a cylindrical was and distributes crushed and the carbon material powder was obtained. The peak intensity ratio $I(\text{C}:101) / I(\text{C}:100)$ was measured from the X-ray diffraction pattern of this powder. Moreover, the boron content was measured. The boron content of the post-baking of the sample of 0, 2, 4, 6 wt% was the respective 0.1.2, 2.5, and 4.3wt% to the addition boron concentration.

It well mixed after adding boron powder (the purity 99.9%, and 325mesh less than) in silicon powder (the purity 99.9%, and 325mesh less than) with 10, 22, 38, 54, 60, 68wt%. This mixture was sealed in the graphite scull of a cylindrical and it shut tightly to the lid in which a screw stuck. This seal scull was raised temperature to 1385°C with the electric furnace among the argon air current of $10\text{L}/\text{min}$. After it preserved at the ionic degree with 10 hour, it cooling-emited to the near room temperature. At this time, the average cooling rate from 1385°C to 600°C was about $33^\circ\text{C}/\text{min}$. After the obtained powder was pulverized with the impeller mill, the powder less than 325mesh was obtained. The peak intensity ratio $I(\text{SiB}_4:021) / I(\text{Si}:111)$ was measured from the X-ray diffraction including this sample etc. The boron content among this powder was measured. Then, the boron amount of addition the thermal process of the sample, and the boron content after a pulverizing which was 10, 22, 38, 54, 60, 68wt% were the respective 10, 21, 37, 52, 59, 66wt%. This thermal process furnace the addition boron nearly like that remained behind.

It well mixed after adding boron powder (the purity 99.9%, and 325mesh less than) in silicon powder (the purity 99.9%, and 325mesh less than) with 45 weight%. 23 hours mechanical alloying processing was handled by using the ball mill this mixture. It raised temperature to

1385°C and thereafter it preserved at the ionic degree like above statement among the argon air current of 10L / min with 1 hour. It cooled to the room temperature with about 3 hour. After the obtained powder was pulverized with the impeller mill, the powder less than 325mesh was obtained. The peak intensity ratio $I(SiB_4:021) / I(Si:111)$ was measured from this sample X-ray diffraction. The boron content among this powder was measured. Then, the boron content was 44wt%. The addition boron nearly like that remained behind to this processing.

<The preparation of the compound powder>

In the large size beaker, the ethanol about 1kg and the boron which in the above case, was obtained were contained or 500g was charged by the sum of the powder of 2 kind of the carbon material powder which it did not contain and the silicon material powder containing the boron which in the above case, was obtained. After it agitated in the room temperature with White heat hour, the compound powder performing 24 hours vacuum dry the powder on the filter paper which absorbed and filters by using the filter paper and remained to 100°C was obtained. This compound powder changed the powder and mixing ratio of the mixing former and it manufactured with plural species.

<Holotrichia and electrode evaluation examination of an electrode>

The carbon material powder and the silicon material powder shown in the table 1 were mixed with predetermined amount. The carbon content x (wt%) among the obtained compound powder, the content z1 (wt%) of the boron existing among the boron content z (wt%), and the silicon material powder within a z, and the content z 2 (wt%) of the boron existing among the carbon material powder were shown in the table 1. Moreover, as the rate of these element contents, it was the C1= z1 (y+z1), the C2 = (y+z1) / (x+y+z), and the peak intensity ratio at the C3= z2 / (x+z2) and X-ray diffraction. The I1= $I(SiB_4:021) / I(Si:111)$, and I2 = $I(C:101) / I(C:100)$ showed in the table 1. Moreover, in this way, the compound powder as the active material for the lithium ion secondary battery cathode manufactured was used and it did like below and an electrode was prepared. The evaluation examination was performed. The value of as a result (the discharge capacity, the initial efficiency, and a cycleability) showed for the table 1.

PVdF was used in the negative active material powder as a binder. NMP the coating liquid was produced as a solvent. This was coated with on the Cu sheet and the electrode sheet of about 0.1mm thickness was prepared with the press. It cut off with 1cm×1cm and the cathode electrode was prepared. The spread density was done by about 1.3g / cm³.

In order that the electrode characteristic at the unipolar of the cathode electrode was evaluated, 3 pole equation cell using the lithium metal as the Euphorbiae pekinensis Radix, and the reference pole was used. In an electrolyte, it used as the mixed solvent (1:1 mixing with the volume ratio) of the diethylene carbonate and ethylene carbonate to dissolve the LiCl₄ to the rate of 1mol / l/6. It altogether performed about the rechargeable test under the electric potential regulation to the constant current (0.5mA/cm²) with a charge, and a discharge. 100 time *** a charging/discharging the potential window is done by 2.0 V (the lithium metal standards) in 0V.

Using this electrode evaluation examination, the maximum discharge capacity evaluated as the discharge capacity per the compound powder 1g, and charge and discharge efficiency with the charging/discharging of 1 time, what is called, the initial efficiency, and the rate (cycleability) of the discharge capacity of the compound powder 1g per of 100 time about the maximum discharge capacity per the compound powder 1g were measured.

As to such sample disclosed in the embodiments 4 through 10, the boron inclusion rate among

the boron contain silicon material powder is in range of 50 weight% through 0.1. The ratio I (SiB₄:021) / I (Si:111) is 1 or less. And the mixing ratio of the silicon material powder among the compound powder is altogether satisfied the condition of $0.01+0.1\times C1 \leq C2 \leq 0.15+C1$.

The discharge capacity altogether exceeded 372mAh / g/6 which was the theory capacity of the graphite about the electrode evaluation of this sample. The high value more than the initial efficiency drawing 90% was besides that shown. Moreover, it had the tendency that a cycleability was a little bit degraded as the discharge capacity was enlarged. But 80% or greater of the maximum discharge capacity was secured after the rechargeable cycle of 100 time. The cycleability of being excellent was shown.

In the meantime, as to such sample disclosed in 6 through the comparative example 3, the boron inclusion rate among the boron contain silicon material powder exceeded 50 weight%. Moreover, the mixing ratio of the silicon powder among the compound powder was not altogether satisfied the condition of $0.01+0.1\times C1 \leq C2 \leq 0.15+C1$.

As to the comparative example 3, and the sample of 4, the mixing ratio C2 of the boron contain silicon powder material among the compound powder was $C2 \leq 0.01+0.1\times C1$. These discharge capacities were low. It was lower than that of the theory capacity of the graphite. Moreover, the initial efficiency showed the high value of 90% either before or after. It showed the cycleability of being high more than 90% of the maximum discharge capacity after the rechargeable cycle of 100 time. But the discharge capacity which is less than the theory capacity of the graphite did not have the conventional graphite system cathode material and the big difference. It was difficult to select for material having with fascination.

Moreover, as to the comparative example 5, and the sample of 6, the mixing ratio C2 of the boron contain silicon powder material among the compound powder was $0.15+C1 \leq C2$. That discharge capacity exceeded 372mAh / g/6 which was the theory capacity of the graphite. It showed the high value of the initial efficiency drawing 90% either before or after. But a cycleability was remarkably degraded. It did not have after especially, the rechargeable test of 100 time about 70% of the maximum discharge capacity. For this reason, such material is regarded as the material in which the application of the practical cell is considerably difficult.

Embodiment 11.

It manufactured whether it limped with the lithium ion second of the cylindrical of 18650 type by using the sample of the embodiment 9. The rechargeable test of 500 time was performed, consequently the discharge capacity of 500 time showed the cycleability of being high called 71% of the maximum discharge capacity. Moreover, a battery after a test was disassembled. Then, the electrode material wound with the spiral shape like that preserved the shape. The part which specially degraded was not recognized.

실험 예	탄소분말 중의 부소합유량(wt%)	규소분말 중의 부소합유량(wt%)	x(wt%)	y(wt%)	z(wt%)	z1(wt%)	z2(wt%)	C1	C2	C3	I1	I2	방전 용량 (mAh/g)	초기� 용 량(%)	사이클 특성(%)
	4	0	10	93.4	5.3	0.6	0.6	0	0.10	0.06	0	0.06	2.2	460	90.3
실험 예 5	0	10	89.6	9.1	1.0	1.0	0	0.10	0.10	0	0.06	2.2	550	90.1	90
실험 예 6	1.2	10	79.5	17.2	3.0	2.0	1.0	0.10	0.19	0.012	0.06	2.6	750	91.5	83
실험 예 7	0	10	77.8	19.9	2.1	2.1	0	0.10	0.22	0	0.06	2.2	810	90.2	82
실험 예 8	0	21	89.2	8.1	2.2	2.2	0	0.21	0.10	0	0.24	2.2	490	91.7	93
실험 예 9	0	37	89.5	6.2	3.7	3.7	0	0.37	0.10	0	0.71	2.2	410	91.0	94
실험 예 10	2.5	41	86.9	5.8	6.8	4.6	2.2	0.44	0.10	0.025	0.99	3.1	400	92.6	93
비교 예 3	0	59	94.5	2.1	3.0	3.0	0	0.59	0.05	0	1.74	2.2	320	90.3	94
비교 예 4	4.3	66	90.4	1.8	7.6	3.5	4.1	0.66	0.05	0.043	2.19	3.6	290	88.8	95
비교 예 5	0	52	22.5	37.3	39.8	39.8	0	0.52	0.77	0	1.34	2.2	390	92.1	69
비교 예 6	2.5	52	11.4	42.6	45.8	45.5	0.3	0.52	0.88	0.026	1.34	3.1	400	91.0	71

■ Effects of the Invention

According to the present invention, while the high discharge capacity is realized, the high initial efficiency, the secondary lithium battery having a cycleability and the thus used anodal active material can be provided. In case of using silicon material containing moreover, the boron as the anodal active material for the secondary lithium battery, it is incongruent for the generated mass production. The anodal active material for the secondary lithium battery solving the problem that generates the big capacity loss in a charging/discharging and it cannot obtain in the discharge volume and lower than the graphite system carbonaceous material that a reversibility is worse than and the secondary lithium battery which is comprised by using this is provided.

The present invention is to provide the active material for the secondary lithium battery cathode in which the practicality resolving swelling and shrinking problem of following moreover, a charging/discharging is high it has the initial efficiency and the cycleability of being high it moreover realizes the discharge capacity exceeding 372mAh / g/6 which is the theory capacity of the graphite and the secondary lithium battery which is comprised by using this.



Scope of Claims

Claim[1] :

The anodal active material for the secondary lithium battery of the silicon material powder it is comprised of the silicon material powder containing the boron, wherein the boron content is 50 weight% through 0.1.

Claim[2] :

The anodal active material for the secondary lithium battery of claim 1, wherein 50% accumulation diameter (d_{50}) of the anodal active material is $100 \mu\text{m}/6$ through 1.

Claim[3] :

The anodal active material for the secondary lithium battery of claim 1, wherein as to the anodal active material is the X-ray wide-angle diffraction method, the ratio $I(\text{SiB}_4:021) / I(\text{Si}:111)$ of the peak intensity $I(\text{SiB}_4:021)$ of the diffracted ray from (021) side of the SiB_4 about the peak intensity $I(\text{Si}:111)$ of the diffracted ray of (111) side of Si is 1 or less.

Claim[4] :

The anodal active material for the secondary lithium battery of the silicon material powder the boron is contained, wherein the boron content is 50 weight% through 0.1, and the carbon material powder does not contain.

Claim[5] :

The anodal active material for the secondary lithium battery of claim 4, wherein 50% accumulation diameter (d_{50}) of the anodal active material is $100 \mu\text{m}/6$ through 1.

Claim[6] :

The anodal active material for the secondary lithium battery of claim 4, wherein as to the anodal active material is the X-ray wide-angle diffraction method, the ratio $I(\text{SiB}_4:021) / I(\text{Si}:111)$ of the peak intensity $I(\text{SiB}_4:021)$ of the diffracted ray from (021) side of the SiB_4 about the peak intensity $I(\text{Si}:111)$ of the diffracted ray from (111) side of Si is 1 or less.

Claim[7] :

The anodal active material for the secondary lithium battery of claim 4, wherein it is the carbon material powder in which the carbon material powder does not contain the boron; and the ratio $I(\text{C}:101) / I(\text{C}:100)$ with the peak $I(\text{C}:100)$ of the diffracted ray from (100) side of the peak intensity $I(\text{C}:101)$ of the diffracted ray from (101) side of the carbon and carbon are 1 or greater

within the diffraction peak measured at moreover, the X-ray wide-angle diffraction method of the compound powder.

Claim[8] :

The anodal active material for the secondary lithium battery wherein it is the carbon material powder in which the carbon material powder contains the boron; and the rain I (C:101) / I (C:100) of the peak I (C:100) of the diffracted ray from (100) of the peak intensity I (C:101) of the diffracted ray from (101) side of the carbon and carbon are 2 or greater within the diffraction peak measured at moreover, the X-ray wide-angle diffraction method of the compound powder.

Claim[9] :

The secondary lithium battery of the silicon material powder it is comprised of the anodic active material, and the silicon material powder, wherein the boron content is 50 weight% through 0.1, and as to the silicon material powder, the anodal active material contains the boron as to the lithium secondary electron containing the anodal active material and non-aqueous electrolyte.

Claim[10] :

The secondary lithium battery of claim 9, wherein 50% accumulation diameter (d_{50}) of the anodal active material is $100 \mu\text{m}/6$ through 1.

Claim[11] :

The secondary lithium battery of claim 1, wherein as to the anodal active material is the X-ray wide-angle diffraction method, the rain I (SiB_4 :021) / I (Si:111) of the peak intensity I (SiB_4 :021) of the diffracted ray from (021) side of the SiB_4 about the peak intensity I (Si:111) of the diffracted ray is 1 or less from (111) side of Si.

Claim[12] :

The secondary lithium battery of the silicon material powder it is comprised of the anodic active material, the carbon material powder, and the silicon material powder containing the boron, wherein the boron content is 50 weight% through 0.1, and as to the carbon material powder, the anodal active material contains the boron as to the secondary lithium battery containing the anodal active material and non-aqueous electrolyte or which it does not contain.

Claim[13] :

The secondary lithium battery of claim 12, wherein 50% accumulation diameter (d_{50}) of the anodal active material is $100 \mu\text{m}/6$ through 1.

Claim[14] :

The secondary lithium battery of claim 12, wherein as to the anodal active material is the X-ray wide-angle diffraction method, the rain I (SiB_4 :021) / I (Si:111) of the peak intensity I (SiB_4 :021) of the diffracted ray from (021) side of the SiB_4 about the peak intensity I (Si:111) of the diffracted ray from (111) side of Si is 1 or less.

Claim[15] :

The secondary lithium battery in which it is the carbon material powder; and the rain I (C:101) / I (C:100) with the peak I (C:100) of the diffracted ray from (100) side of the peak intensity I (C:101) of the diffracted ray from (101) side of the carbon and carbon are 1 or greater within the diffraction peak measured at moreover, the X-ray wide-angle diffraction method of the compound powder of claim 12, wherein the carbon material powder does not contain the boron.

Claim[16] :

The secondary lithium battery of claim 12, wherein it is the carbon material powder in which the carbon material powder contains the boron; and the rain I (C:101) / I (C:100) with the peak I

(C:100) of the diffracted ray from (100) side of the peak intensity I (C:101) of the diffracted ray from (101) side of the carbon and carbon are 2 or greater within the diffraction peak measured at moreover, the X-ray wide-angle diffraction method of the compound powder.

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(54) 영상분석을 이용한 대기중 먼지 측정 방법

요약

먼지를 포함하는 대기는 영상을 왜곡하는 작용을 한다. 이 방법은 영상분석을 이용하여 대기중 먼지량을 측정한다. 이 방법은 실시간 측정이 가능하고 사용하는 필터를 교환함으로써 다양한 크기의 대기중 먼지량을 측정할 수 있다.

레이저 광원을 이용하여 특정 영상을 만들고, 이 영상을 왜곡이 적고 반사율이 우수한 거울에 반사시켜 대기를 통과시킨다. 완전히 여과한 공기를 사용하여 먼지가 없는 대기를 통과시켰을 때의 표준영상을 얻어 디지털 영상 파일로 저장하고, 외부의 대기를 사용하여 얻어지는 영상도 디지털 영상 파일로 저장한다. 표준 영상과 외부 대기를 통과한 영상을 비교하여 영상이 왜곡되는 정도를 화소 단위로 정량한다. 이러한 영상왜곡정도는 대기에 존재하는 먼지량에 비례므로 대기중 먼지량을 측정할 수 있다. 외부의 대기를 사용할 때 필요한 크기의 기공 크기(pore size)를 갖는 필터를 사용함으로써 먼지의 입경별로 먼지량도 측정할 수 있다.

대표도
 도 1

색인어
 영상 분석, 대기오염, 먼지, 거울

명세서

도면의 간단한 설명

도 1은 본 발명에 의한 측정기기의 설계도이다.

발명의 상세한 설명

발명의 목적

발명이 속하는 기술 및 그 분야의 종래기술

본 발명은 대기오염지표 중 먼지를 측정하는 방법에 관한 것으로 보다 정확하고 쉽게 대기중 먼지를 측정하는 방법에 관한 것이다.

먼지는 다양한 크기를 갖는 대기오염물질이다. 먼지는 다양한 환경문제와 건강문제의 원인이 된다. 따라서 대기중 먼지를 측정하는 것이 매우 중요하다. 대기중 먼지를 측정하는 기준 방법은 특정 기공 크기(pore size)를 갖는 필터에 대기 를 통과시켜 그 필터에 걸려진 먼지량을 측정하는 방법이다. 이 방법은 일정 시간 대기 포집이 필요하며 필터에 걸려진 먼지를 분석하는 시간이 소요된다는 문제점이 있다. 또 다른 측정 방법인 산란계(nephelometer)는 먼지 오염에 의한 시정 측정에 사용되나 빛의 감쇠 정도를 광센서로 측정함으로써 소량의 먼지오염이나 특정 크기의 입경을 갖는 먼지량을 민감하게 측정하지 못한다는 제한점이 있다.

발명이 이루고자 하는 기술적 과제

본 발명은 이러한 문제점을 해결하기 위해 안출된 것으로서 대기중에 존재하는 먼지량을 짧은 시간과 적은 비용으로 정확히 측정하는 방법을 제공하는 것을 그 기술적 과제로 한다.

발명의 구성 및 작용

상기 기술적 과제를 달성하기 위한 본 발명은 대기중에 존재하는 먼지는 황사 현상이 있을 때 시야가 부옇게 되는 것과 같이 영상의 왜곡을 일으킨다는 점을 이용한다. 이러한 영상의 왜곡은 대기중 존재하는 먼지의 양에 비례하므로 영상 왜곡 정도를 정밀하게 정량적으로 측정하면 대기중 존재하는 먼지의 양을 측정할 수 있다.

이하 첨부된 도면을 참조하여 본 발명을 보다 상세하게 설명한다.

원거리를 투과하여도 영상의 왜곡이 거의 없는 레이저 광원을 이용한 영상을 발생시킨다. 이 영상을 본 발명에서 창안한 측정기기 안에서 습도, 온도, 기류, 조도 등이 표준화된 조건하에서 대기를 필요한 거리만큼 투과시키며, 필요한 거리만큼 대기를 투과시키기 위해 반사율과 화면왜곡이 적은 거울을 이용한다. 이 단계에서 필요할 경우 왜곡이 적은 확대경을 사용하여 영상을 확대한다. 대기중 먼지량이 적어서 화면 왜곡이 너무 적게 나타날 경우 측정기 내부 압력을 올려 대기중 먼지 농도를 농축시키면 더 적은 양의 먼지도 감지할 수 있다. 거울을 반사하며 대기를 투과하고 필요한 경우 확대된 영상을 디지털 영상장치를 이용하여 디지털 영상파일로 변환, 저장한다.

필터를 통해 먼지를 완전히 제거한 공기를 측정기기 안에 넣어 얻은 표준 영상 파일과 먼지를 포함한 외부 공기를 측정 기기 안에 넣어 얻은 영상 파일을 비교하여 영상 왜곡 정도를 화소 단위로 산출한다. 대기중 먼지를 측정하는 다른 장비를 사용하여 영상 왜곡 정도와 대기중 먼지 존재량 사이의 관계식을 작성한다. 이 관계식에 따라 영상 왜곡 정도로써 대기중 먼지량을 산출한다. 측정기기 안에 넣을 공기를 특정 크기의 기공을 갖는 필터로 거른 다음 영상왜곡정도를 측정하면 특정 크기의 입경을 갖는 공기중 먼지량도 측정할 수 있다.

발명의 효과

본 발명에 의한 대기중 먼지 측정방법은 기존 방법에 비해 시간이 적게 걸리고 측정기기의 가격이 낮을 것으로 기대된다.

또한 본 발명에 의한 방법은 대기 통과 거리를 거울을 사용하여 원하는 만큼 늘려 줄 수 있고, 측정장치 내부 압력을 올림으로써 필요한 만큼 대기중 먼지를 농축할 수 있으므로 적은 양을 대기중 먼지도 측정할 수 있다는 장점이 있다.

또한 특정 기공크기의 필터를 선별적으로 사용함으로써 다양한 입경의 대기중 먼지도 함께 측정할 수 있다는 장점이 있다.

(57) 청구의 범위

청구항 1.

표준적인 조건하에서 먼지가 포함된 대기를 투과한 영상의 왜곡 정도를 디지털 영상 분석을 통해 정량적으로 측정하는 방법

청구항 2.

충분한 양의 대기를 투과시키기 위해 측정기기안에 거울을 사용하여 대기 투과거리를 늘려주는 방법

청구항 3.

특정 기공 크기를 갖는 필터를 사용하여 공기를 걸러 줌으로써 특정 입경 크기의 먼지를 측정하는 방법

청구항 4.

대기중 먼지를 농축시키기 위해 측정장치 내부 압력을 높여주는 방법

도면

도면 1

